

Chapter 4

Discussion

Iron

The theoretical dilution curves from field investigations and mixing experiments during wet and dry seasons are illustrated in Fig. 5 and 6 respectively.

Iron is present in "dissolved" form in river waters at concentrations higher than those found in seawater. It was found that behaviour of iron in estuary is important because of its influence on removal of organic matter, aggregation of suspended particles, scavenging of heavy metals, and possible regulation of phosphate levels. (Smith and Milne, 1981). The observed levels of dissolved iron is dependent on the pore-size of the filter used. It was concluded that at least half the iron in river water filtered through a conventional 0.45 μm -filter was colloidal which has a large effective surface area (Smith and Milne, 1981).

Generally, iron transported by rivers undergoes changes resulting in the formation of flocs and in some sequence sedimentation (Coonley et al., 1971; Windom et al., 1977; Sholkovitz et al., 1978) The results of this study (Fig, 5; 6) shows an increase in iron concentration in the suspended particulate matter up to salinity 10 ‰, with decreasing iron content at higher salinity. With the exception of mixing experiment in dry season that show an increase in particulate iron concentration at above a salinity of 10 ‰. The mixing experiments, in fact, should represent the actual mixing of the Mae Klong River Water and seawater without any influence from additional end member, industrial and domestic

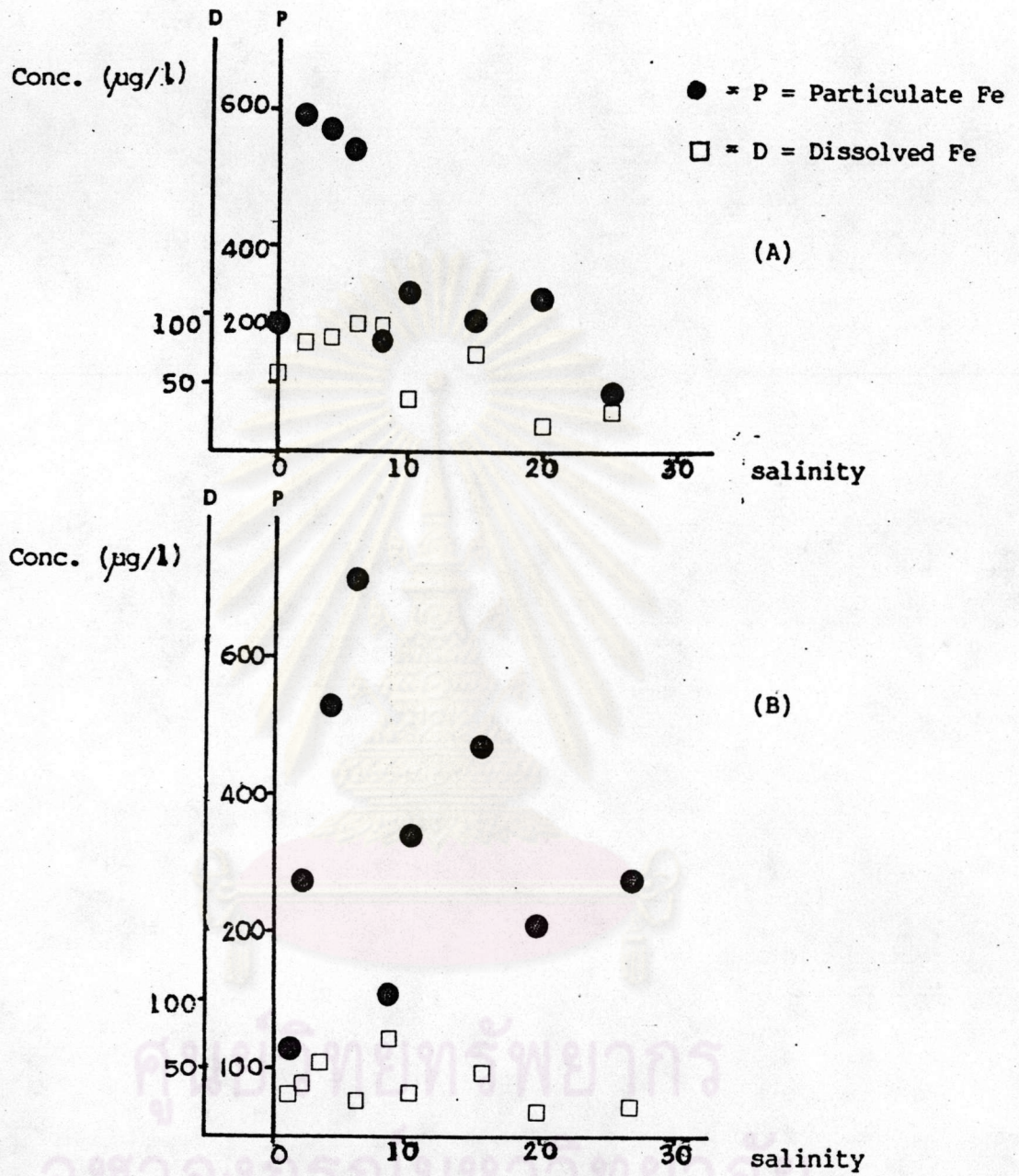


Fig. 5 Iron concentration as a function of salinity in dry season
 (A) = from the Mae Klong River, and (B) = mixing experiment.

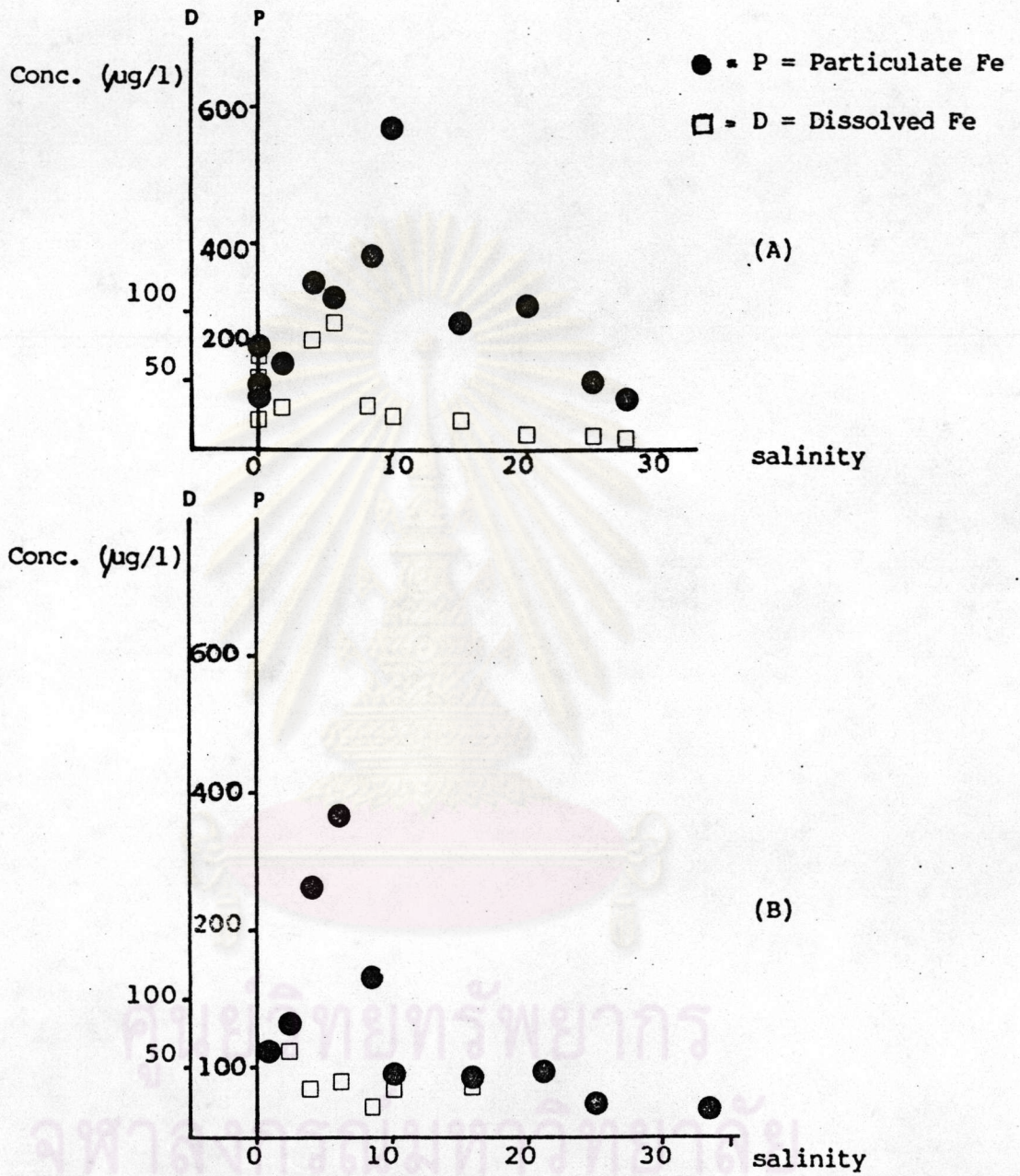


Fig. 6 Iron concentration as a function of salinity in wet season
 (A) = from the Mae Klong River, and (B) = mixing experiment.

wastes. Therefore, one should be able to observe a mixing behaviour of iron resulting from two end members.

The results of mixing experiment in both dry and wet seasons show an increase in particulate iron concentration at salinity lower than 10 ‰ with the maximum at about 8 ‰. Theoretically, dissolved iron (III) in river water can be hydrolyzed. The hydrolysis of dissolved iron is dependent on pH of the solutions. Estuaries are transition area between river-water pH values, typically 6.0 - 7.0, and that of sea-water ~ 8.1 . Thus, it is within estuary that formation of new solid phases, e.g. oxides and hydroxides of iron, might be expected to occur. Losses of dissolved iron during estuarine mixing by this process have been described by many investigators, such as Windom et al. (1976), Holliday and Liss (1976).

One should also note that the mixing experiment of this type, the particulate metal concentration is always decreased by the dilution effect. This is because starting with two end members, river water and seawater, the volume ratio of river water : seawater will decrease as the salinity of the mixed solution increases.

The particulate iron concentration above salinity 10 ‰ from mixing experiments in two seasons differs dramatically. It appears that the removal of dissolved iron is likely to be more extensive in wet season than in dry season. There are two possible explanations: (1) the presence of larger amount of suspended load carrying by the Mae Klong River during wet season together with larger volume of river water; (2) the use of sea-water end member of different origin. The presence of particulate matter was shown to increase the removal of dissolved iron from river waters, and this effect was greater than the one produced by increasing the salinity (Aston and Chester, 1973).

Therefore, during wet season, the removal of dissolved iron should be completed at the salinity about 8 ‰. while the decrease in particulate iron concentration, at above the salinity 8 ‰. should result from dilution of a more turbid river water with seawater. The result of the mixing experiment in dry season shows an additional increase in particulate iron concentration at 15 ‰. The phenomena is abnormal and theoretically unexplainable.

The results of field investigations are far more complicated by the introduction of, at least, two additional end members namely freshwater from Klong Ampawa and Klong Dumnernsaduak and the introduction of industrial and domestic waste discharging into the Mae Klong River.

Iron behaves differently during two seasons. As has been mentioned previously about locations of sampling, one should bear in mind that the river-water end member of wet season is different from the one in dry season. This is because the river-water end member of wet season was collected at Samut Songkram city, therefore, there would be no additional end member in this case. In addition, the samples collected during wet season should be under strong influence of the domestic waste from Samut Songkram.

In wet season, the removal of dissolved iron, as shown by highest particulate iron concentration, occurs at salinity of 10 ‰. At above 10 ‰, the particulate iron concentration decreases as the salinity increases. The variation of particulate concentration with salinity observed is quite reasonable. It does show a removal of dissolved iron at low salinity while the decrease of particulate iron concentration at higher salinity is a result of physical mixing. However, when one observes dissolved iron, it shows that iron is added to the dissolved form at low salinity (below 6 ‰). This is probably

indicating an increase in solubility of iron by organic ligands in river water (Picard and Felbeck, 1976). Phosphate in domestic waste may complicated this additional/removal processes of iron further. It was found that dissolved iron was removed by the association between phosphorus and iron-organic colloid at low salinity while either at higher salinity or at lower levels of dissolved phosphate, this association would be reversed (Boyle et al, 1977).

The field investigation during dry season shows a more complicated behaviour. Though, particulate iron concentration is at its highest at salinity 2 ‰, the removal process may not be completed yet. This can be seen from the increase in particulate iron concentration at salinity 10 ‰ and 20 ‰. However, it can be said that the particulate iron concentration in this season tends to decrease with an increasing degree of dilution by seawater. The two additional end member of river water from Klong Dumnernsaduak and Klong Ampawa may account for the increase in particulate iron concentration at the salinity of 10 ‰ and 20 ‰ by reinitiating the precipitation of oxide and hydroxide of iron. The dilution curve of this season shows the increase in dissolved iron at the salinity of 10 ‰ and 15 ‰. This increase is likely to result from process of resolubilization of iron by organic ligand at salinity below 10 ‰ and changes in physico-chemical conditions of the Mae Klong River water upon the introduction of two additional end members.

The organic matter found in aquatic system consists of the remains of biologically produced compounds as well as of synthetic organic substances. The most important products formed during the decomposition of organic substances are the humic substances. Humic substances are a major component of the dissolved organic carbon and

particulate organic carbon in freshwater (Nissenbaum and Swaine, 1976). Synthetic organic substances originate from industrial and agricultural application. They are those of high molecular weight which can be decomposed mostly due to microbiologic actions, thus forming a smaller and more soluble fragment.

These organic substances, particularly humic substances can sorp trace elements such as Cu, Co, Mn, Fe, Cd etc. effectively (Rachid, 1971). It was suggested that portions of many trace metals present in natural waters as a soluble organic complex is generally greater than that present as the inorganic or the aqua complex (Jenne, 1976). Humic substances are flocculated during estuarine mixing (Stumm and Morgan, 1981), thus, being removed from water. The maximum amount of removal is found to be between salinities of 15 ‰ and 20 ‰ (Sholkovitz, 1976). However, humic substances in dissolved form are capable of : (1) Complexing metals and increasing solubility; (2) Altering the distribution between oxidised and reduced forms of metals; (3) influencing the extent to which metals are adsorped on suspended matter, and (4) affecting the stability of metal-containing colloids (Singer, 1977). Therefore, it is obvious that removal of organic matter is very important in the study of mixing behaviours of metals. At lower salinities (ca. below 20 ‰), it present can either inhibit or enhance the removal process of dissolved metals or vice versa.

In this study, the removal of iron from river water, particularly at low salinity, occurs. This removal process may be inhibited by the presence of dissolved organic matter in the Mae Klong River water. The behaviour of iron during estuarine mixing varies from season to season under the influence of discharge, both in terms of volume of water and amount of suspended load, amount and type of domestic and industrial wastes.

It is well established that adsorption of trace elements from solution onto mineral and organic solids takes place in natural waters (cf. Kraufkopt, 1956; Turekian, 1971). Trace element adsorption results from several mechanisms including electrostatic extraction, changes in the hydration states of the adsorbate, covalent bonding, Van de Waal's bonding and hydrogen bonding (Aston, 1978). Mineral and other solid particles suspended in natural water carry an electrical surface charge, so that attraction and surface adsorption of charged species from solution is a wide spread mechanisms by which solid-solution exchange can occur. This form of interaction is rapid and readily reversible, and may be postulated as an important process by which cationic and anionic trace element species are adsorbed by or desorbed from, suitably charged particles.

In an estuarine situation, suspended solids capable of providing adsorption sites are subjected to important physico-chemical changes which result from the mixing of river- and sea-waters. These changes influence the adsorption/desorption behaviour of the suspended matter and modify the colloidal nature of much of it. Thus, estuaries represent a situation in which the solid-solution enrichment or depletion of the trace element content of either suspended particles or the "dissolved" constituents of estuarine water. Exchange reactions are obviously major factors in the control of the form in which elements are transported from the continent to the oceans and marine sediment.

Aston (1978) categorized the solid-solution exchanges processes in estuaries into 2 groups corresponding to an adsorption or desorption effects;

1. Exchange of trace elements between pre-existing solid and solution

2. precipitation of dissolved matter to give new solid phases

The process of trace metal solid-exchange at solid-solution interface is affected by the following factors; (Forstner and Wittman, 1981)

1. Detrital mineral. The presence of a large portion of detrital minerals in particulate matter results in characteristics enrichment of trace elements, particularly in the fine-grained particulate matter

2. Sorption. Solids can sorp every trace element effectively and a generalized sequence of the capacity of solids to sorp trace elements was established by Guy and Chakrabarti (1975):

$\text{MnO}_2 \succ \text{humic acids} \succ \text{iron oxides} \succ \text{clay minerals}$

The sorption processes on solid surface can be ion exchange, chemical sorption and organic complexation

3. Coprecipitation with hydrous Fe/Mn oxide and carbonate.

Hydrous iron and manganese oxides constitute a highly method sink for trace elements. Coprecipitation with CO_3 may be an important mechanism for trace element removal when hydrous irons or organic oxides or organic substances are less abundant

4. Complexation and flocculation with organic matter. Inorganic systems the role of iron and manganese as direct adsorbants of trace element ions is either over shadowed by competition from the more reactive humic acids and organo-clays, or is obscured by coating of organic matter (Jonasson, 1977). Once the trace elements are complexed by humic acids, the solutions behave as if other ions were not present in the reaction media. The sequence of complexability between trace elements and humic substances has been established by the results of studies of Rachid (1974), Jonasson (1977);

$\text{Cu} \succ \text{Pb} \succ \text{Ni} \succ \text{Co} \succ \text{Zn} \succ \text{Cd} \succ \text{Fe} \succ \text{Mn} \succ \text{Mg}$

It showed that copper is preferentially sorbed while lead sorption onto

organic substances is influenced by pH (Rachid, 1974).

5. Metal precipitating. At present, the extent of direct precipitation of trace element hydroxides, carbonates and sulphides as yet to be observed, it is assumed that the composition of these precipitates is greatly influenced by various hydro-chemical conditions of the water body in question, and is subjected to waste disposal.

In the estuarine mixing zone, the significant of these mechanisms and their respective substrates for trace elements has been estimated. The processes of flocculation of metal-organic complexes and coprecipitation with metal hydrous, Fe/Mn oxides are expected to be the most important processes while uptake by organism seem to be particular important especially to those trace elements introduced by human activities (Forstner and Wittman, 1981).

Copper

The results of mixing experiment, which are shown in fig 7b and 8b for dry and wet season respectively, show a seasonal variation in copper behaviour. In dry season, particulate copper concentration are high at salinity of 10 ‰ and 20 ‰. While in the wet season, it is at salinity of 6 ‰. In comparison, the removal of copper during wet season, showing the same trend as mixing experiments of iron during wet season, is more extensive than in dry season. The result indicates the removal of dissolved copper to be the result of coprecipitation of copper with iron oxides at low salinity. The decrease in particulate copper concentration found in the mixing experiment at the salinity above 6 ‰ in wet season is likely to be caused by dilution effect. However, if one compares the change in dissolved copper concentration with salinity from mixing experiment in both seasons, it is found that

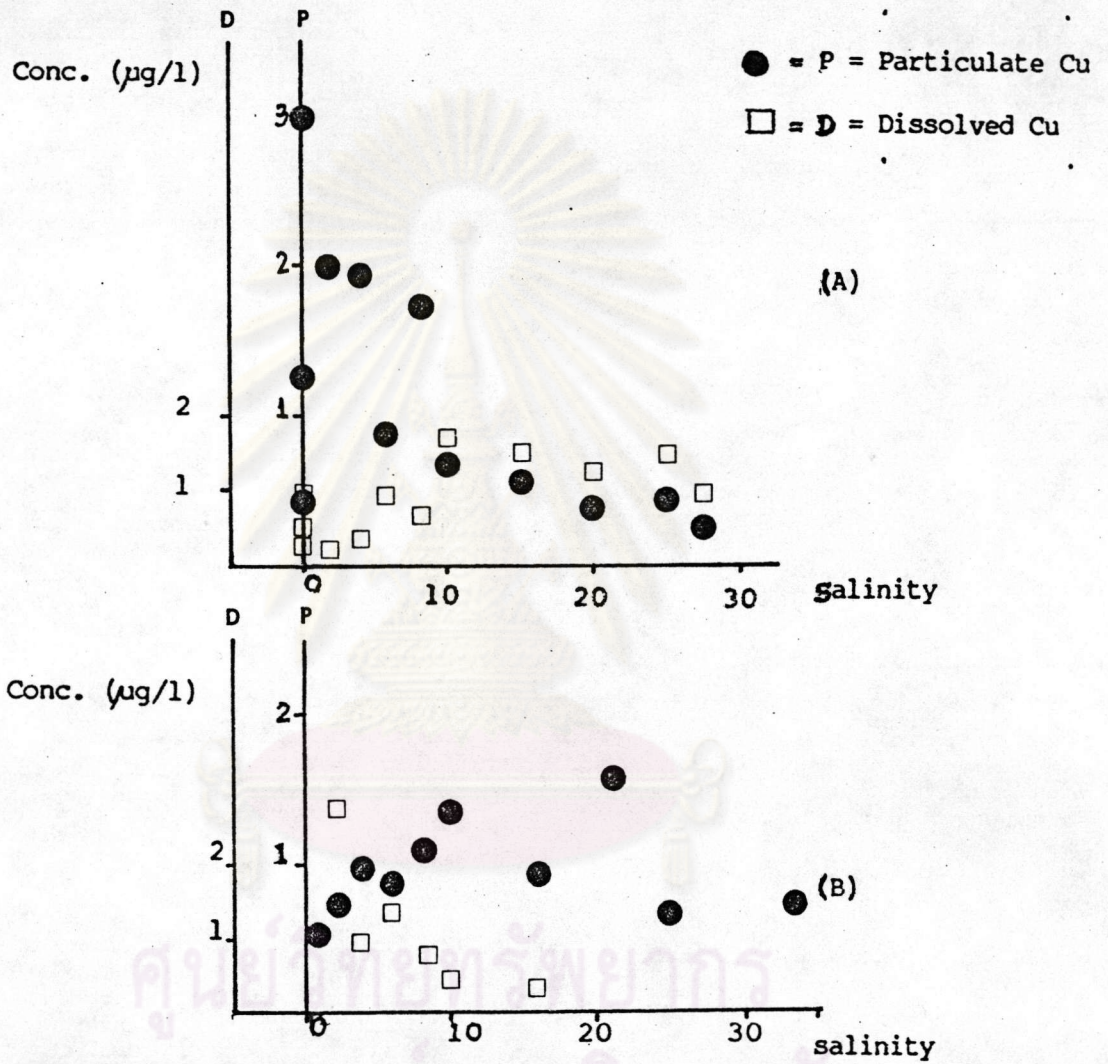


Fig. 7 Copper concentration as a function of salinity in dry season
 (A) = from the Mae Klong River, and (B) = mixing experiment.

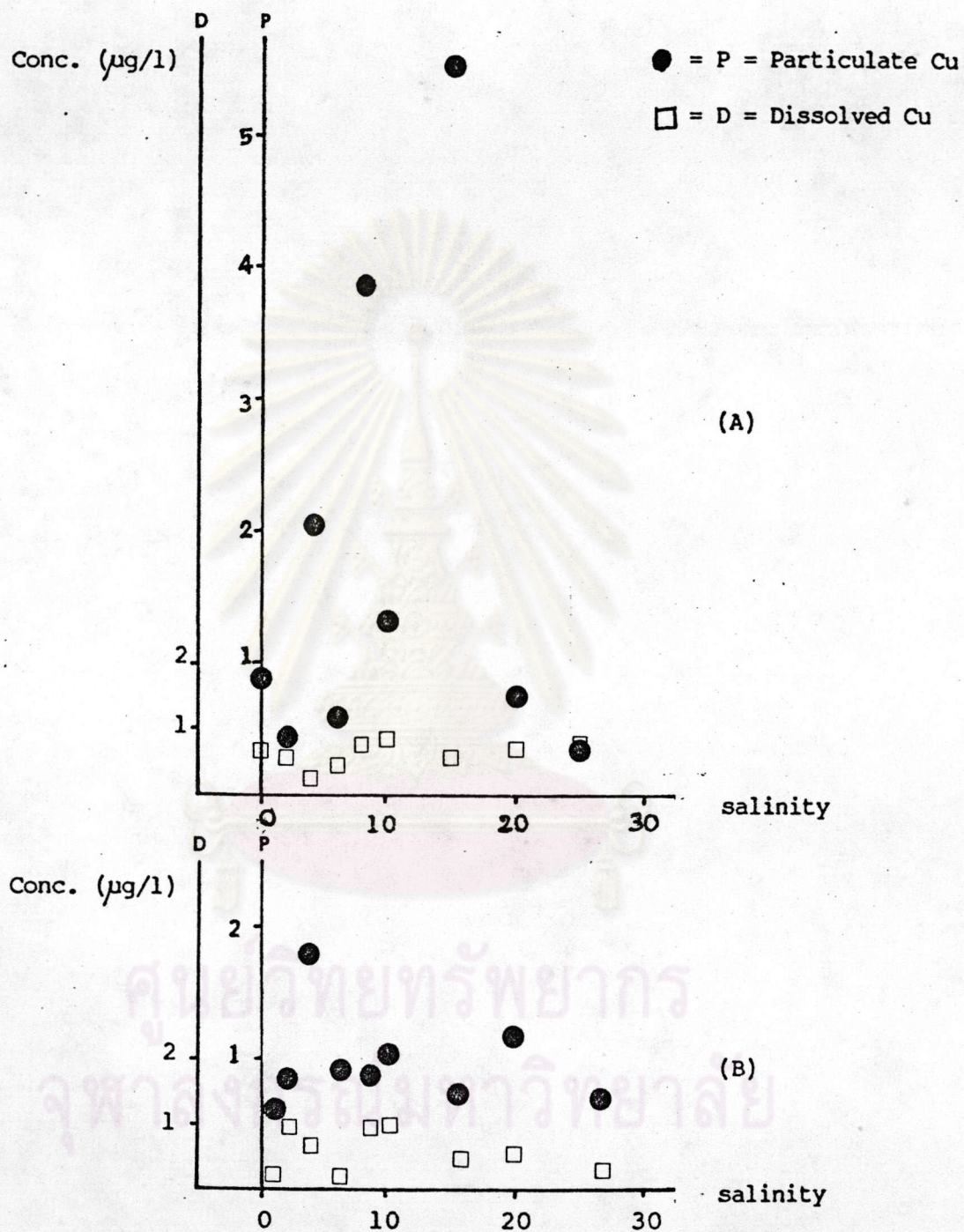


Fig. 8 Copper concentration as a function of salinity in wet season
(A) = from the Mae Klong River, and (B) = mixing experiment.

dissolved copper concentration is more or less constant than those found in dry season. This finding confirms a more extensive removal of dissolved copper in wet season at every salinity, while in the dry season, the dissolved copper is removed gradually as the salinity increases. This phenomena was also observed by Duinker and Nolting (1977), in the Rhine estuary.

The results of field investigations (fig. 7a, 8a) show that copper behaves differently in wet and dry seasons. During wet season, the highest particulate copper concentration was found at salinity of 15 ‰. While in the dry season, it was found at salinity of 2 ‰. If one uses the dilution curve approach for these two field investigations, some common trends emerge. Dissolved copper concentration in both seasons exhibit a minimum in concent at salinity below 4 ‰. This minimum is likely to be related to adsorption or to a changes in a form of copper to an analytically undetectable form such as metal-organic complexes (Bewers and Yeats, 1976). At salinity above 10 ‰, in both seasons, the addition of dissolved copper occurs. This addition is less pronounced in wet season probably because of larger volume of river-water. This addition is expected to be the contribution of copper desorped from river borne particles (Thomus and Grill, 1977). Another interesting point is the mixing behaviour of copper, particularly in dry season, does not seem to be affected by additional river-water end member as in the case of iron. This is probably because copper can either be adsorbed or be complexed with high stability (Rachid, 1974; Jonasson, 1977).

Lead

From results of mixing experiments in both seasons, dissolved

lead seems to be removed at low salinity (10 ‰ in dry season; 6 ‰ in wet season). The desorption of lead is found in wet season at salinity of 20 ‰. However, from both mixing experiments, it is very difficult to use the product approach for interpretation of the mixing behaviour of Pb, as the particulate lead concentrations do not show a clear trend of increase or decrease when plotted against salinities. By using the variation of dissolved lead concentrations against salinities, it is found that the removal processes occur in both seasons seem to be coincided with the removal of iron in each season respectively. Therefore, removal of dissolved lead by coprecipitation of iron oxides should be predominant in both season (fig. 9a, 10a). The mixing behaviour of lead found during field investigations indicating non-conservative behaviour in both seasons. In addition, lead behaves differently in wet and dry seasons. In wet season, the decrease in dissolved lead concentrations with increase in salinity indicates removal process. In dry season, addition of dissolved lead concentrations was found at low salinity (below 6 ‰). Removal is found at salinity of 15 ‰ and another addition was found at salinity of 25 ‰. It is very likely that the behaviour of lead concentration is under strong influence : - coprecipitation with iron oxides at below 6 ‰, - desorption which caused by the changes in physico-chemical conditions upon the introduction of additional river-water end member at salinity between 10 to 15 ‰; - release interstitial water upon the resuspended of sediment in the estuary (at salinity of 25 ‰).

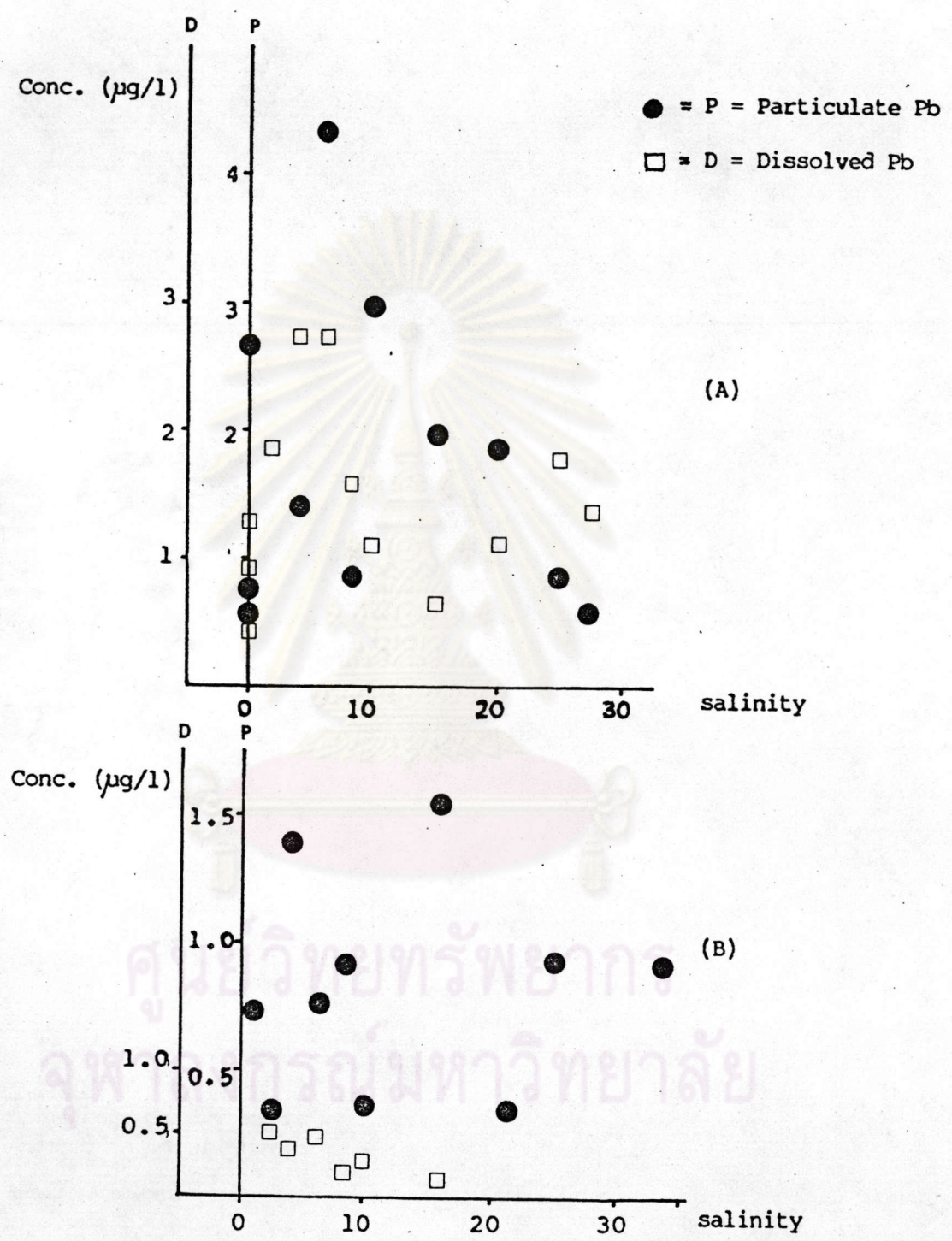


Fig. 9 Lead concentration as a function of salinity in dry season
(A) = from the Mae Klong River, and (B) = mixing experiment.

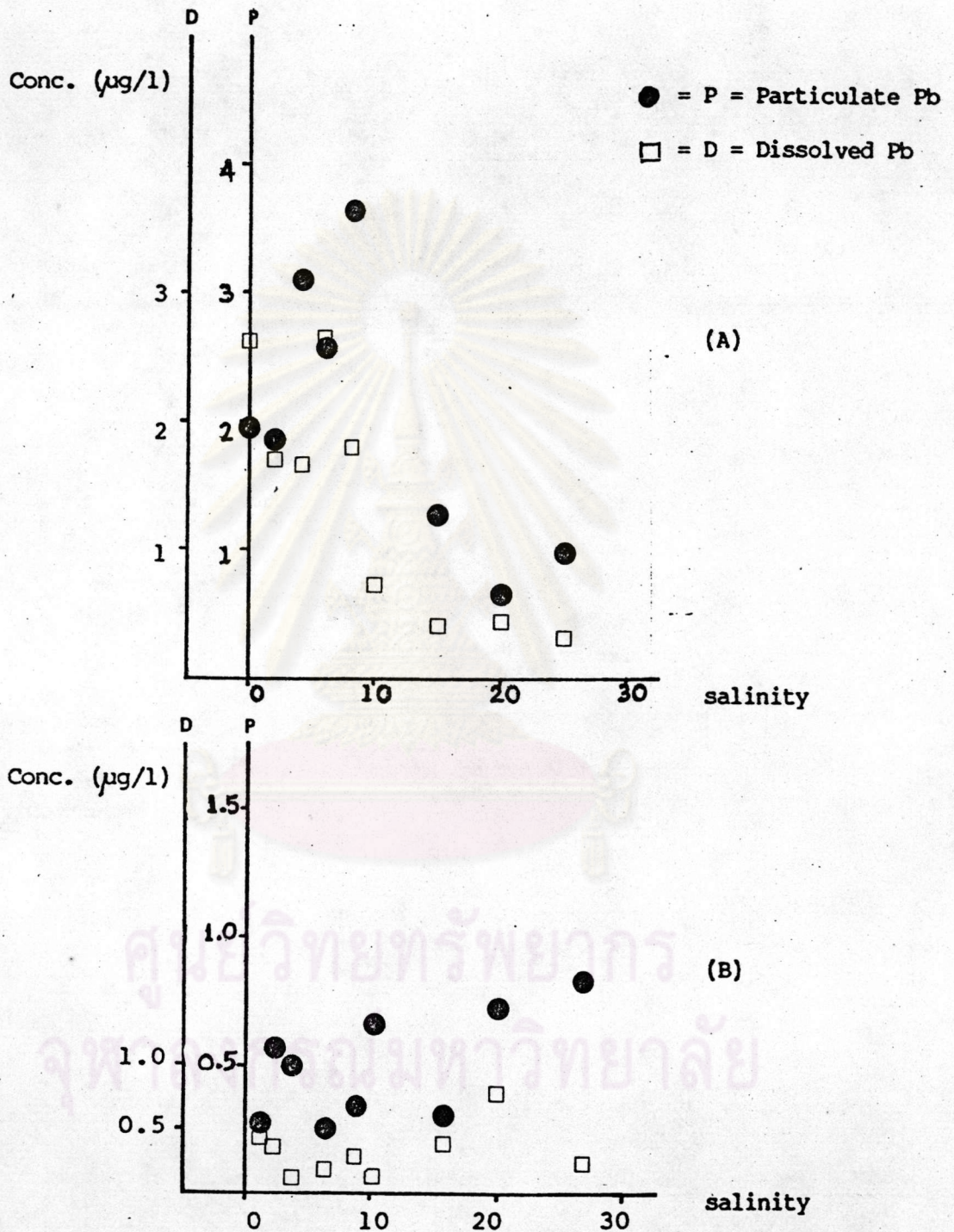


Fig. 10 Lead concentration as a function of salinity in wet season
 (A) = from the Mae Klong River, and (B) = mixing experiment.